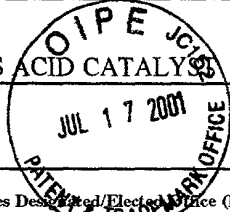


FORM PTO 190  
(REV 4-99)

US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY DOCKET NUMBER  
2001-1009ATRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371U.S. APPLICATION NO.  
(if known, see 37 CFR 1.5)  
[NEW] 09/889406International Application No.  
PCT/JP00/07386International Filing Date  
October 23, 2000Priority Date Claimed  
November 17, 1999Title of Invention  
POLYMER-SUPPORTED LEWIS ACID CATALYSTApplicant(s) For DO/EO/US  
Shu KOBAYASHI

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:


1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. §371(c)(2)). **ATTACHMENT A**
  - ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)).
    - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☐ have been transmitted by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☐ have not been made and will not be made.
  - ☐ A translation of the amendments to the claims under PCT Article 19.
9. ☒ An unexecuted oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). **ATTACHMENT B**
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 14. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98. **ATTACHMENT C**
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment. **ATTACHMENT D**
  - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☒ Other items or information:
  - a. International Search Report - **ATTACHMENT E**

09/889406

JC17 Rec'd PCT/PTO 17 JUL 2001

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) [NEW]		INTERNATIONAL APPLICATION NO. PCT/JP00/07386		ATTORNEY'S DOCKET NO. 2001-1009A	
15. [X] The following fees are submitted				CALCULATIONS	PTO USE ONLY
<b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1000.00 International Search Report has been prepared by the EPO or JPO ..... \$ 860.00 International preliminary examination fee not paid to USPTO but international search paid to USPTO ..... \$ 710.00 International preliminary examination fee paid to USPTO but claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$ 690.00 International preliminary examination fee paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$ 100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).					
Claims	Number Filed	Number Extra	Rate		
Total Claims	8 -20 =	0	X \$18.00		
Independent Claims	1 -3 =	0	X \$80.00		
Multiple dependent claim(s) (if applicable)			+ \$270.00		
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$860.00	
[ ] Small Entity Status is hereby asserted. Above fees are reduced by 1/2.					
<b>SUBTOTAL =</b>				\$860.00	
Processing fee of \$130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+	
<b>TOTAL NATIONAL FEE =</b>				\$860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40 per property +					
<b>TOTAL FEES ENCLOSED =</b>				\$860.00	
				Amount to be refunded	\$
				Amount to be charged	\$
a. [X] A check in the amount of \$ <u>860.00</u> to cover the above fees is enclosed. A duplicate copy of this form is enclosed. b. [ ] Please charge my Deposit Account No. 23-0975 in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0975</u> .					
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or          (b)) must be filed and granted to restore the application to pending status.</b>					
19. CORRESPONDENCE ADDRESS			By: <u>Matthew Jacob</u> Matthew Jacob, Registration No. 25,154  WENDEROTH, LIND & PONACK, L.L.P. 2033 "K" Street, N.W., Suite 800 Washington, D.C. 20006-1021 Phone: (202) 721-8200 Fax: (202) 721-8250  July 17, 2001		
 000513 PATENT TRADEMARK OFFICE					

THE COMMISSIONER IS AUTHORIZED  
TO CHARGE ANY DEFICIENCY IN THE  
FEES FOR THIS PAPER TO DEPOSIT  
ACCOUNT NO. 23-0975

[CHECK NO. 45486]

[2001-1009A]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Shu KOBAYASHI

Serial No. [NEW]

Filed July 17, 2001

POLYMER-SUPPORTED LEWIS ACID  
CATALYST

[Corresponding to PCT/JP00/07386  
Filed October 23, 2000]

Attn: BOX PCT

Docket No. 2001-1009A

THE COMMISSIONER IS AUTHORIZED  
TO CHARGE ANY DEFICIENCY IN THE  
FEES FOR THIS PAPER TO DEPOSIT  
ACCOUNT NO. 25-0975

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents,  
Washington, DC 20231

Sir:

In the interest of compact prosecution and to reduce PTO filing fees, please amend the present application as follows:

IN THE CLAIMS:

*Please amend claims 5-7 as follows:*

5. (Amended) The polymer-supported Lewis acid catalyst according to claim 1, wherein the polymeric chain comprises a polymer obtained by the addition polymerization of aromatic monomers.

6. (Amended) The polymer-supported Lewis acid catalyst according to claim 1, wherein the polyvalent element (M) is a lanthanoid element.

7. (Amended) A method of organic synthesis using the polymer-supported Lewis acid catalyst according to claim 1, wherein the reaction is performed in water or an aqueous medium.

REMARKS


The above amendment is presented to eliminate multiple dependent claims, thereby reducing PTO filing fees.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is entitled "**Version with Markings to Show Changes Made**".

Favorable action on the merits is now requested.

Respectfully submitted,

Shu KOBAYASHI

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July 17, 2001

## VERSION WITH MARKINGS TO SHOW CHANGES MADE

### IN THE CLAIMS:

*Claims 5-7 have been amended as follows:*

5. **(Amended)** The polymer-supported Lewis acid catalyst according to [any one of claims] claim 1 [to 4], wherein the polymeric chain comprises a polymer obtained by the addition polymerization of aromatic monomers.

6. **(Amended)** The polymer-supported Lewis acid catalyst according to [any one of claims] claim 1 [to 5], wherein the polyvalent element (M) is a lanthanoid element.

7. **(Amended)** A method of organic synthesis using the polymer-supported Lewis acid catalyst according to [any one of claims] claim 1 [to 6], wherein the reaction is performed in water or an aqueous medium.

POLYMER-SUPPORTED LEWIS ACID CATALYST

Technical Field

The present invention relates to a polymer-supported Lewis acid catalyst. Particularly, the present invention relates to a novel Lewis acid catalyst, which shows high reactivity even in aqueous medium without the use of organic solvents, is easily prepared and recovered, and is excellent in reusability, and to methods of organic synthesis using such novel Lewis acid catalyst.

Background Art

The execution of organic synthesis in aqueous medium without the use of harmful organic solvents has long been a major object in industry.

Heretofore, various methods of reaction in aqueous mediums containing organic solvent have been proposed, but none have been practical; one major reason being that in reactions performed in aqueous mediums, organic compounds are not soluble in water.

In order to solve such problems, the inventors of the present invention have developed Lewis acid-surfactant linked catalysts comprising scandium, tris(dodecylsulfate), scandium tris(dodecylsulfonate) or the like (Kobayashi, S., Wakabayashi, T., Tetrahedron Lett. 1998, 39, 5389; Kobayashi, S., Chem. Lett.

1991, 2187; Kobayashi, S., Nagayama, S., Busujima, T., J. Am. Chem. Soc. 1998, 120, 8287).

It has been said that by using such catalysts, organic compounds would quickly dissolve in water in a colloidal manner to allow reactions such as the aldol reaction of silyl enole ethers and aldehydes to proceed smoothly, without the use of organic solvents.

Although such substantial improvements were said to be possible, in reality, for the above catalyst, its recovery from water was not necessarily easy; hence, the difficulty in recovering and purifying the reaction products were problematic.

The invention of the present application has been achieved to solve the above-described problems, based on the knowledge on Lewis acid catalysts that enable organic synthesis in aqueous medium, proposed by the inventors, to provide a novel Lewis acid catalyst, which show high reaction activity in aqueous medium, may easily be recovered and is excellent in reusability.

#### Disclosure of Invention

In order to solve the above-described problem, the invention of the present application first provides a polymer-supported Lewis acid catalyst comprising a Lewis acid group expressed by the following general formula (I):





(wherein M represents a polyvalent element, X represents an anionic group, and n is an integer representing the valence of M) linked and supported on a polymeric membrane via a SO<sub>3</sub> or SO<sub>4</sub> group.

Further, the invention of the present application secondly provides the above-described Lewis acid catalyst wherein the Lewis acid group of the following general formula (II):



(wherein M represents a polyvalent metallic element, X represents an anionic group, n is an integer representing the valence of M, and R<sup>0</sup> is a SO<sub>3</sub> or SO<sub>4</sub> group) is linked and supported on a polymeric chain via a spacer chain; provided thirdly, is the polymer-supported Lewis acid catalyst, wherein the spacer chain is a hydrocarbon group; provided fourthly, is the polymer-supported Lewis acid catalyst, wherein the spacer chain is expressed by the following general formula (III):



(wherein Ph represents a phenyl group and m and l each represent an integer of 1 or more).

Furthermore, the invention of the present application provides fifthly, any one of the above-described polymer-supported Lewis acid catalysts, wherein the polymer chain is a polymer obtained by the addition polymerization of an aromatic monomer; provided sixthly, is any one of the

above-described polymer-supported Lewis acid catalysts wherein the polyvalent element (M) is a lanthanoid element.

Furthermore, the invention of the present application seventhly provides an organic synthesis reaction method using any one of the above-described polymer-supported Lewis acid catalysts, wherein the reaction is performed in water or an aqueous medium; and provided eighthly, is the above-described method of organic synthesis, comprising the formation of a carbon-carbon bond.

#### Best Mode for Carrying Out the Invention

In the Lewis acid catalyst of the present invention, a Lewis acid group expressed by the following general formula (I):



is bonded to a polymeric chain. Here, the polyvalent element (M), which constitutes the Lewis acid group, may be chosen from various elements known conventionally to constitute a Lewis acid. For example, various types of elements such as Al, B, Ti, Zr, Sn, Zn, Ga, Bi, Sb, Si, Cd, V, Mo, W, Mn, Fe, Cu, Co, Pb, Ni, Ag, lanthanoid elements and so forth are illustrated. Among these elements, scandium (Sc), lanthanoid elements such as ytterbium (Yb) and lanthanum (La) are especially favorable in the present invention.

The anionic group (X) may be chosen from various types

of anionic groups including those similar to conventional ones. For example, halogen atoms, organic acid groups and the like are included; as an organic acid group, for example, a sulfonic acid group such as trifluoromethane sulfonate (OTf), a phosphoric acid group and the like may be included.

In the present invention, such Lewis acid groups are linked to and supported on a polymeric membrane via a SO<sub>3</sub> (sulfonic acid) group or a SO<sub>4</sub> (sulfuric acid) group.

In such linkage, the polymeric chain or the molecular structure may comprise the direct bonding of the Lewis acid group to the polymeric chain via a SO<sub>3</sub> or SO<sub>4</sub> group, or the bonding of SO<sub>3</sub> or SO<sub>4</sub> group via a spacer molecular chain. In other words, the structure may be expressed by the following general formula (IV):



(wherein R<sup>0</sup> represents a SO<sub>3</sub> or SO<sub>4</sub> group, A<sub>1</sub> represents the polymer chain, and A<sub>2</sub> represents the spacer molecular chain).

Further, the (A<sub>2</sub>-R<sup>0</sup>-MX<sub>n</sub>) structure may be in a state bonded to any desired number of polymer chains. The spacer chain may be constructed taking in consideration such points as the hydrophilic degree, productivity or a catalytic activity.

As the spacer chains, hydrocarbon groups may be illustrated as representative examples. Further, cycloalkyl groups and aryl groups may also be included. These hydrocarbon groups may optionally include substituents, as well. More

specifically, as spacer molecular chains, those expressed by the following general formula (III):



may be exemplified. Here, for example,  $m=1$  to 7 and  $l=1$  to 3 may be preferable.

The polymeric chain on which the Lewis acid catalyst is supported, may be chosen from various types; however, from the viewpoint of production and handling, polymers derived mainly from the addition polymerization of monomers are exemplified as favorable. Among them, aromatic addition polymerization monomers such as styrene,  $\alpha$ -methylene, divinylbenzene and the like are illustrated.

In any of the above-described cases, the polymer chain used in the present invention is a solid substance insoluble in water or aqueous mediums.

As described above, the polymer-supported Lewis acid catalyst of the present invention may be prepared, for example, by allowing the Lewis acid group to bond to a polymer chain or a polymer chain substance comprising a spacer molecular chain, via a  $SO_3$  or  $SO_4$  group. In such case, the  $SO_3$  or  $SO_4$  group may be bonded to the polymeric chain substance in advance, after which the Lewis acid group may be bonded to the  $SO_3$  or  $SO_4$  group, or the Lewis acid group having a  $SO_3$  or  $SO_4$  group may be bonded to the polymeric chain substance. Of course, the polymer-supported Lewis acid catalyst of the present invention

is not limited to the above-described types, and may be prepared by bonding a Lewis acid group to a polymer chain through various processes.

Further, the polymer-supported Lewis acid catalyst according to the present invention may be utilized in various types of organic synthesis reactions to exert the catalytic action of a Lewis acid. In such case, the reaction method is characteristic in that an aqueous medium, namely, water alone, may be used as the reaction medium. Of course, aqueous mediums obtained by mixing organic solvents such as alcohols, THF or other hydrophilic or polar solvents with water may be used; however, the most important characteristic of the polymer-supported Lewis acid catalyst of the present invention is that water alone may be used as the reaction medium, to obtain high reaction activity; further, the catalyst may easily be recovered because it is supported on solid polymer, and the high reaction activity is maintained even after recycling.

For the catalytic action of the Lewis acid catalyst, the polymer-supported Lewis acid catalyst of the present invention may be used effectively as the catalyst for, for example, alkylation reaction, allylation reaction, aldol-type reaction, Diels-Alder reaction, Strecker-type reaction and the like. In each of the above reactions, the reaction medium may be water or an aqueous medium.

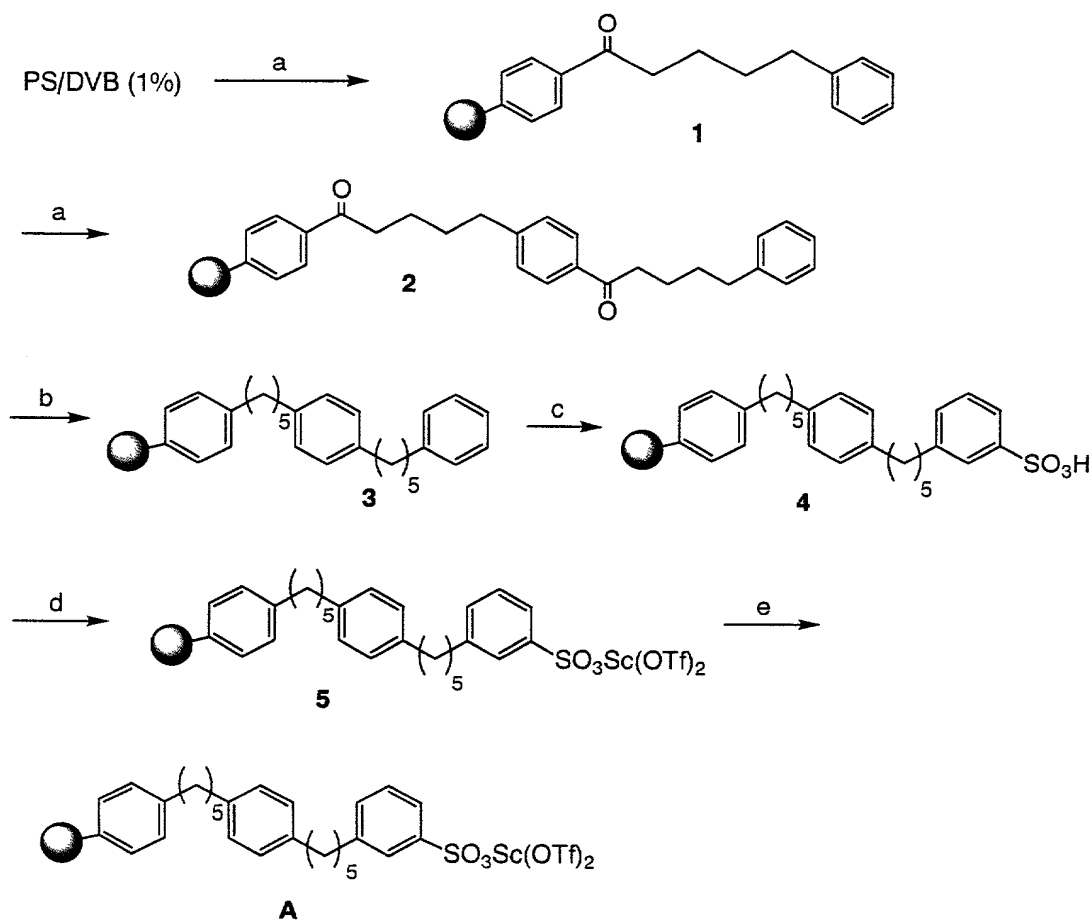
Embodiments of the invention of the present application

are described in more detail through the following examples.

## Examples

### <Example 1>

A polymer-supported scandium catalyst (A) was prepared as a polymer-supported Lewis acid catalyst of the present invention, according to the following reaction scheme:



Namely, firstly,

(a) polystyrene (5.0 g) cross-linked by 1 % divinylbenzene (DVB) was reacted with 5-phenylvaleroylchloride

(Ph(CH<sub>2</sub>)<sub>4</sub>COCl) (4.7 g; 24 mmol) in CS<sub>2</sub> (100 ml) in the presence of AlCl<sub>3</sub> (3.2 g, 24 mmol) at room temperature for 24 hours.

1N HCl (300 ml) was added to the resultant reaction mixture and stirred at the same temperature for 12 hours. Then, the mixture was filtrated, rinsed with H<sub>2</sub>O, H<sub>2</sub>O-THF, THF, and Et<sub>2</sub>O, and then dried under reduced pressure; the ketonic reaction product (1) was obtained.

Identification results of compound (1) are shown in TABLE 1.

TABLE 1

<sup>13</sup>C SR-MAS NMR (CDCl<sub>3</sub>); δ = 24.1, 31.1, 35.8, 40.6, 125.7, 128.3, 128.6, 135.1, 142.2, 145.23, 199.8.

IR (neat) 1679 cm<sup>-1</sup>.

Next, the ketonic product was reacted with 5-phenylvaleroylchloride (4.7 g, 24 mmol) in CS<sub>2</sub> (100 ml) in the presence of AlCl<sub>3</sub> (3.2 g, 24 mmol) and reacted under reflux for 24 hours. After the resultant reaction mixture was cooled to room temperature, 1N HCl (300 ml) was added and stirred for 12 hours. Then, the mixture was filtrated and rinsed with H<sub>2</sub>O, H<sub>2</sub>O-THF, THF, and Et<sub>2</sub>O and thereafter, dried under reduced pressure; the diketone product (2) was obtained.

Identification results of compound (2) are shown in TABLE 2.

TABLE 2

$^{13}\text{C}$  SR-MAS NMR ( $\text{CDCl}_3$ );  $\delta$  = 24.0, 30.6, 31.1, 35.8, 38.1, 40.4, 125.7, 127.9, 128.3, 134.9, 142.2, 145.2, 199.8.

IR (neat)  $1679\text{ cm}^{-1}$ .

(b) The diketone product (2) was reacted with  $\text{AlCl}_3$  (6.4 g, 48 mmol) - LAH (1.9 g, 4.8 mmol) in ether (100 ml) under reflux condition for 12 hours. After the reaction mixture was cooled to  $0^\circ\text{C}$ , 1N HCl (300 ml) was added to the mixture and stirred for 12 hours. Then, the stirred mixture was filtrated and rinsed with  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ -THF, and THF, and thereafter, dried under reduced pressure; the reduction product (3) was obtained.

Identification results thereof are as follows:

TABLE 3

$^{13}\text{C}$  SR-MAS NMR ( $\text{CDCl}_3$ );  $\delta$  = 24.8, 29.0, 31.3, 35.5, 35.9, 40.4, 125.7, 128.2, 139.9, 142.7, 145.5.

(c) The reduction product (3) was reacted with chlorosulfonic acid:  $\text{ClSO}_3\text{H}$  (0.47 g, 4.0 mmol) in dichloromethane (25 ml) at  $0^\circ\text{C}$  for 12 hours. Then, acetic acid (25 ml) was added to the resultant reaction mixture to terminate the sulfonation reaction. The resultant reaction mixture was filtrated then rinsed with  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ -THF, THF, and  $\text{Et}_2\text{O}$ , and thereafter, dried under reduced pressure; the sulfonic acid product (4) was obtained. The supported amount of compound



(4) was confirmed to be 1.29 mmol/g, through acid-base titration. Further, the identification result thereof was IR (neat) 1679  $\text{cm}^{-1}$ .

(d) The sulfonic acid product (4) (1.0 g) was reacted with scandium chloride:  $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$  (370.1 mg) in acetonitrile (10 ml) under reflux for 24 hours. After the resultant reaction mixture was cooled to room temperature, acetonitrile (10 ml) was added, after which the mixture was filtrated and rinsed with acetonitrile, and dried under reduced pressure; the scandium-bonded product (5) was obtained.

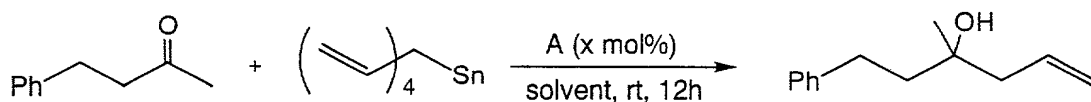
(e) The scandium-bonded product (5) was reacted with trifluoromethane sulfonic acid:  $\text{TfOH}$  (186.7 mg, 1.24 mmol) in dichloromethane (10 ml) at room temperature for 12 hours.

Water (10 ml) was added to the resultant reaction mixture, which was then filtrated, rinsed with  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$ -THF, THF, and  $\text{Et}_2\text{O}$ , and thereafter, dried under reduced pressure; the polymer-supported scandium catalyst (A) was obtained.

Elemental analysis, confirmed the presence of 0.6 % of scandium.

#### <Example 2>

Using the catalyst (A) obtained in Example 1, the allylation reaction of 4-phenyl-2-butanone with tetraallyltin was performed, according to the following reaction scheme:



The reaction was performed in various media including water, at room temperature for 12 hours. In such reaction, 4-phenyl-2-butanone (0.4 mmol) and tetraallylstin (0.2 mmol) were used with a predetermined amount of the catalyst (A). 3 ml of a solvent was used therein. The reaction results are shown in TABLE 4.

TABLE 4

Conditions	Solvents	Catalysts (mol%) <sup>a</sup>	Yields (%)
1	H <sub>2</sub> O	3.2	92 (93 <sup>b</sup> , 90 <sup>c</sup> )
2	H <sub>2</sub> O	1.6	95 (90 <sup>d</sup> , 92 <sup>e</sup> )
3	H <sub>2</sub> O	0.8	84
4	CH <sub>2</sub> Cl <sub>2</sub>	3.2	38
5	CH <sub>3</sub> CN	3.2	15
6	Benzene	3.2	28
7	EtOH	3.2	20
8	DMF	3.2	trace

\* Unless otherwise specified, compound 5 (1.29 mmol/g) was used.

<sup>a</sup> determined by elemental analysis of scandium in compound 1

<sup>b</sup> reused (second time) <sup>c</sup> reused (third time) <sup>d</sup> compound 5 (0.52 mmol/g) used

<sup>e</sup> compound 5 (2.46 mmol/g) used.

In the reaction wherein water was used as the reaction medium and 3.2 mol% of the polymer-supported scandium catalyst (A) was used (condition 1), a homoallyl alcohol compound was obtained in a high yield of 92 %. On the other hand, reactions wherein organic solvents were used (conditions 4 to 8) showed

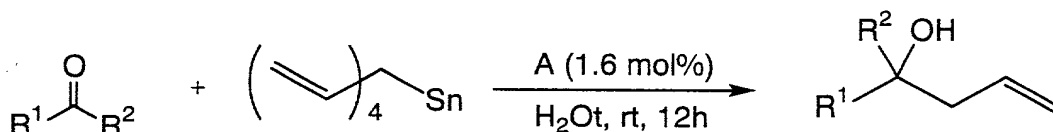
low reaction yield.

Further, with condition 1, even when the catalyst (A) was reused for the second time and, moreover, for the third time, high reaction yields of 93 % and 90 % were obtained, respectively. The process of recovering the catalyst (A) was easy, and only involved filtration.

In addition, in condition 2, a high yield of 95 % was obtained by using 1.6 mol% of the catalyst (A).

#### <Example 3>

As in Example 2, the allylation of various types of aldehyde compounds and ketone compounds were performed in an aqueous medium according to the following reaction scheme:



The reactions were carried out using 1.6 mol% of the above-described catalyst (A) at room temperature for 12 hours. Results are shown in TABLE 5.

TABLE 5

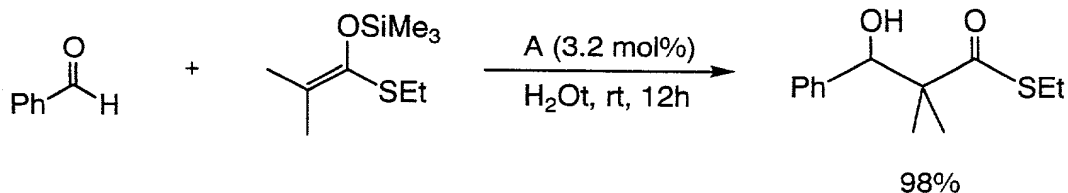
Conditions	R <sup>1</sup>	R <sup>2</sup>	Yields (%)
1	Ph	H	82
2	Ph(CH <sub>2</sub> ) <sub>2</sub>	H	quant
3	c-C <sub>5</sub> H <sub>11</sub>	H	72
4	(E)-PhCH=CH	H	99
5	2-pyridyl	H	83
6	PhCO	H <sup>a</sup>	90 <sup>b</sup>
7	Ph(CH <sub>2</sub> ) <sub>2</sub>	Me	quant
8	(E)-PhCH=CH	Me	91
9	Ph	CO <sub>2</sub> Et	90

<sup>a</sup> Monohydrate    <sup>b</sup> diallylation product obtained

Each reaction showed a high yield.

#### <Example 4>

Using 3.2 mmol% of the above-described polymer-supported scandium catalyst (A), benzaldehyde and 1-ethylthio-1-trimethylsiloxy-2-methylpropane were reacted in 5 ml of aqueous medium at room temperature for 12 hours according to the following reaction scheme:



As a result, the corresponding aldol-type reaction product was obtained in a high yield of 98 %.

When the amount of catalyst (A) was decreased to 1.6 mol%, the yield was 77 %.

Identification results of the product, S-ethyl-3-hydroxy-2,2-dimethyl-3-phenylpropanethioate, are shown in TABLE 6.

TABLE 6

S-Ethyl-3-hydroxy-2,2-dimethyl-3-phenylpropanethioate

$^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  = 1.05 (s, 3H), 1.15 (s, 3H), 1.18 (t, 3H, 7.4 Hz), 2.81 (q, 2H, 7.4 Hz), 2.90 (br, 1H), 4.87 (s, 1H), 7.19-7.25 (m, 5H).

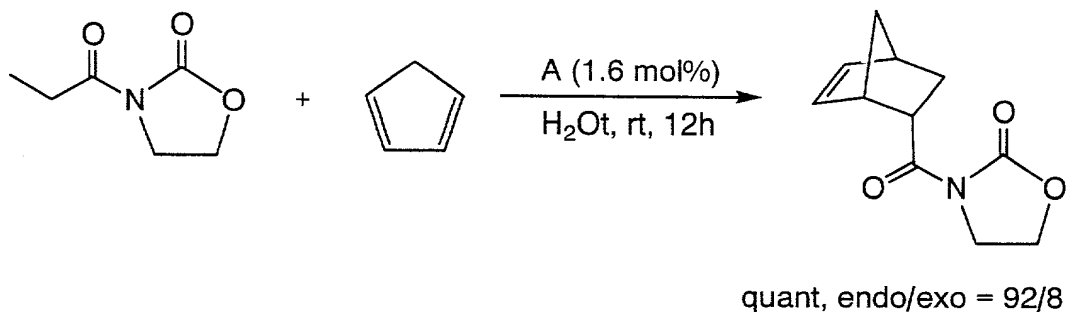
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ );  $\delta$  = 14.4, 20.0, 23.3, 23.6, 54.3, 78.9, 127.7, 127.8, 139.9, 207.9.

<Example 5>

As in Example 1, a polymer-supported ytterbium catalyst was prepared, using ytterbium (Yb) instead of scandium, and used in a reaction similar to that of Example 4. The reaction performance obtained was approximately equivalent to that obtained for Example 4.

<Example 6>

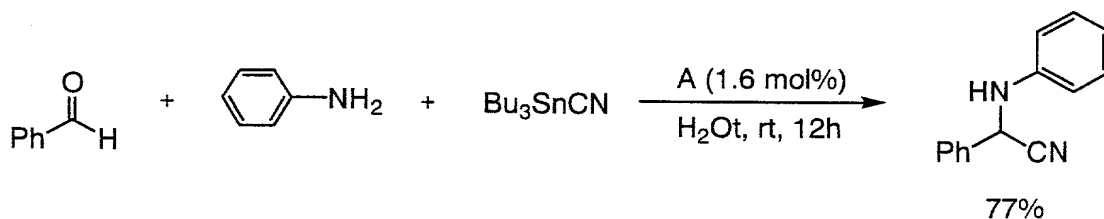
Using 1.6 mol% of the above-described catalyst (A), the Diels-Alder reaction of 3-acroxy-1,3-oxazolidine-2-one and cyclopentadiene was performed in an aqueous medium at room temperature for 12 hours according to the following reaction scheme:



The adduct: 3-(bicyclo[2,2,1]hepta-5-ene-2-yl)-1,3-oxazolidinone-2-one was obtained quantitatively (endo/exo = 92/8) as the reaction product.

#### <Example 7>

Using 1.6 mol% of the above-described catalyst (A), a Strecker-type reaction of benzaldehyde, aniline, and tributyltin cyanide was performed in an aqueous medium according to the following reaction scheme. The reaction was carried out at room temperature for 12 hours.



The corresponding  $\alpha$ -aminonitrile; 1-phenyl-1-phenylaminonitrile was obtained in a 77 % yield.

Identification results thereof are shown in TABLE 7.

TABLE 7

1-Phenyl-1-phenylaminonitrile

$^1\text{H}$  NMR ( $\text{CDCl}_3$ );  $\delta$  = 4.20 (d, 1H, J. = 9.23 Hz), 5.61 (d, 1H, J. = 9.24 Hz), 6.75-6.78 (m, 2H), 6.88-7.00 (m, 2H), 7.22-7.36 (m, 6H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ );  $\delta$  = 46.04, 104.5, 114.5, 117.5, 126.7, 127.1, 127.2, 129.5, 136.7, 144.0.

Industrial Applicability

As described above in detail, the invention of the present application provides a novel Lewis acid catalyst, which shows high reaction activity in aqueous medium, is easily recovered, and is excellent in reusability, as well as a method of organic synthesis using such novel catalyst.

## CLAIMS

1. A polymer-supported Lewis acid catalyst comprising a Lewis acid group expressed by the following general formula (I):



(wherein M represents a polyvalent element, X represents an anionic group, and n is an integer representing the valence of M) linked and supported on a polymer film via a SO<sub>3</sub> or SO<sub>4</sub> group.

2. The polymer-supported Lewis acid catalyst according to claim 1, comprising the Lewis acid group expressed by the following general formula (II):



(wherein M represents a polyvalent metallic element, X represents an anionic group, n is an integer representing the valence of M, and R<sup>°</sup> represents a SO<sub>3</sub> or SO<sub>4</sub> group) linked and supported on a polymeric chain via a spacer chain.

3. The polymer-supported Lewis acid catalyst according to claim 2, wherein the spacer chain is a hydrocarbon group.

4. The polymer-supported Lewis acid catalyst according to claim 3, wherein the spacer chain is expressed by the following general formula (III):



(wherein Ph represents a phenyl group, and m and l each represent



an integer greater than or equal to 1.)

5. The polymer-supported Lewis acid catalyst according to any one of claims 1 to 4, wherein the polymeric chain comprises a polymer obtained by the addition polymerization of aromatic monomers.

6. The polymer-supported Lewis acid catalyst according to any one of claims 1 to 5, wherein the polyvalent element (M) is a lanthanoid element.

7. A method of organic synthesis using the polymer-supported Lewis acid catalyst according to any one of claims 1 to 6, wherein the reaction is performed in water or an aqueous medium.

8. The method of organic synthesis according to claim 7, which comprises the formation of a carbon-carbon bond.

## ABSTRACT

In order to provide a novel Lewis acid catalyst, which shows high reaction activity in aqueous medium, is easily recovered, and is excellent in reusability, a Lewis acid group expressed by the general formula (I):



(wherein M represents a polyvalent element, X represents an anionic group, and n is an integer representing the valence of M)

is linked and supported on a polymer membrane via an  $\text{SO}_3$  or  $\text{SO}_4$  group.

#3

## DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

( ) Original ( ) Supplemental ( ) Substitute (X) PCT ( ) DESIGN

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: POLYMER-SUPPORTED LEWIS ACID CATALYST

of which is described and claimed in:

- ( ) the attached specification, or  
 ( ) the specification in application Serial No. \_\_\_\_\_, filed July 17, 2001, and with amendments through \_\_\_\_\_, or  
 (X) the specification in International Application No. PCT/JP00/07386, filed October 23, 2000, and as amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
Japan	1999-327424	November 17, 1999	Yes

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

And I hereby appoint Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Warren M. Cheek, Jr., Reg. No. 33,367; Nils Pedersen, Reg. No. 33,145; Charles R. Watts, Reg. No. 33,142; and Michael S. Huppert, Reg. No. 40,268, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., as well as any other attorneys and agents associated with Customer No. 000513, to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys and agents named herein to accept and follow instructions from NISHIZAWA & ASSOCIATES as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

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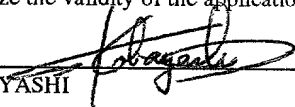
  

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Post Office Address	ADDRESS	CITY	STATE OR COUNTRY ZIP CODE

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor Shu KOBAYASHI  Date Aug 7, 2001  
2nd Inventor \_\_\_\_\_ Date \_\_\_\_\_  
3rd Inventor \_\_\_\_\_ Date \_\_\_\_\_  
4th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
5th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
6th Inventor \_\_\_\_\_ Date \_\_\_\_\_

The above application may be more particularly identified as follows:

U.S. Application Serial No. \_\_\_\_\_ Filing Date July 17, 2001

Applicant Reference Number 00-F-009PCT-US/SH Atty Docket No. 2001-1009A

Title of Invention POLYMER-SUPPORTED LEWIS ACID CATALYST